DEVELOPMENT OF ELECTRON DEFICIENT RECEPTORS FOR HAZARDOUS ANIONS: SENSING AND SELECTIVITY STUDIES

A SYNOPSIS

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1. INTRODUCTION

The development of simple and effective chemo sensors for selective detection of hazardous anions is really challenging area of research in the field of synthetic anion receptor chemistry [1-5]. Further, designing a selective colorimetric sensor for a particular anion is even a complicated one since anions have different shapes and charges [6]. Among the hazardous anions, cyanide ion is one of the most poisonous anions because trace amounts of its presence lead to deactivate many biological processes such the activity of cyto-c and cellular respiration. Cyanide is extensively used in industries such as in metal mining and electroplating process. The extensive usage of cyanide in the industry also increases the risk of environmental pollution [7]. Of several bio relevant anions, Fluoride is the smallest anion that has a high charge density, it is an appealing target for molecular recognition designs because of its association with a wide range of biological, medical, and technological processes [8]. F^- is a typical ingredient found in toothpaste, medicines, and even a drinking water [9]. An excessive amount of fluoride causes Fluorosis, urolithiasis, or even cancer [10]. Among the different anions, particularly, alkali metal - azides are quickly reacting and potentially poisonous chemical that exists as an odorless white solid. When alkali azide is mixed with water or acid, changes immediately into a poisonous gas with very intense odor. Sodium azide also converted in to $HN{=}N^+{=}N^-$ (hydrazoic acid) which is a poisonous gas, when it comes in contact with metals. Furthermore, peoples who are working in automobile industries are at an increased risk of exposure to sodium azide, which is commonly used as a propellant in vehicle's airbags. Sodium azide is also widely used in the syntheses of various chemical components.

Selective anion receptor design is a quiet challenge for researchers. In the supramolecular concept, the host-guest anionic complexes required the combination of the binding site, which is specifically made up of hydrogen-bonding groups The anion receptors have a suitable framework on which different structural components can be assembled. and it needs the combination of hydrogen bond donor groups such as amide, urea, thiourea, sulfonamide, amine. Pentafluoro phenyl moiety functionalization of receptors allows for new anion-receptor interactions, including anion-pi interactions. In this connection, I have designed and synthesized the bipodal and tripodal receptors.

Pentafluoro phenyl moiety functionalization of receptors allows for new anion-receptor interactions, including as anion-pi interactions. Theoretically, a chemo sensor's selectivity and sensitivity will increase if an electron-withdrawing moiety is substituted on the aromatic ring, according to Benjamin Hay [11]. From this concept, I have designed and synthesized the receptors L^1 to L^5 it is able to sense fluoride, cyanide and azide anions selectively. Bryans and Hay [12] report uncovers electron pulling out replacement on the receptor construction can upgrade the acidic idea of the hydrogen bond donors.

2. REVIEW OF LITERATURE

At the beginning time of anion recognition electrostatic interactions are used to interact anion via positive charged centers. The first macrocyclic anions receptors with electrostatic interactions were reported by Park and Simmons [13]. Franz and Schmidtchen detailed one more report which was macrocyclic cage in view of electrostatic interaction was designed [14]. The first neutral tripodal receptors with hydrogen donors and received interaction with anions was reported by Reinhoudt *et al.* [15]. Ghosh *et al.* [16] reported the impact of nitro replacement on direction of the receptor by self-assembly with anions. Anions with nitrated phenylhydrazine based receptors was reported by Shao *et al.* [17]. However, nitro functionalization enhances the sensitivity of the receptor part which leads to lack of selectivity. Tripodal structure with amide and thiourea and nitro aromatic functional in their three arms was reported by Sahoo *et al.* [18]. In 1993, Schneider *et al.* reported first report regarding anion - π interaction [19]. In 2007, Lakshminarayanan *et al.* designed a tripodal frame to captured the anions through π-hole-anion-π-hole interactions. Tris(2-aminoethyl) amine used to construct tripodal frame with fluorinated and non-fluorinated phenyl rings was reported by Ghosh *et al.* [20]. Kathiravan *et al* [21] 2014; Musib *et al* [22] 2020; Zhao *et al* [23] 2014; Lin *et al* [24] 2019; Gao and Zhong [25] 2017 reported that, several types of organic compounds were utilized as fluorescent sensors for detecting anionic species through aggregation-induced enhanced emission (AIEE) phenomenon, whereas upon binding of guest species, the emission of normal fluorophore would be quenched, in particular, at higher concentration level.

3. OBJECTIVES

1. Design and syntheses of simple, effective, colorimetric, and fluorescent anion selective receptors for environmentally relevant anions.

2. Anion binding studies of anion selective receptors

   (a) Naked-eye colorimetric sensing studies

   (b) UV-Vis and fluoro spectrometric studies

   (c) Spectrometric (^{1}H-NMR, FT-IR) studies, of the above synthesized receptors and those anionic complexes.

3. Molecular electrostatic surface analysis (MEP) of anionic complexes.

4. RESEARCH PROBLEM

Design and syntheses simple and effective colorimetric, and fluorescent receptors for anions. To achieve selective recognition of environmental and biologically important anions. To achieve these objectives, all possible experimental and spectroscopic studies are done and discussed in detail.

5. ORGANIZATION OF THESIS

The thesis entitled "DEVELOPMENT OF ELECTRON DEFICIENT RECEPTORS FOR HAZARDOUS ANIONS: SENSING AND SELECTIVITY STUDIES". The thesis is composed of nine chapters.

The research presented in this thesis show hydrazine-based imine, urea, thiourea, and amide, functionalized receptors having electron-withdrawing natured substituents at phenyl moiety show binding towards cyanide, fluoride, and azide anions.

Chapter I contains a general introduction of the thesis and Chapter II describes a literature survey of previous studies of the anion receptors has been reported and the objectives of the current work are discussed. in detail. Chapter III to VIII describes the results and discussion about the as-prepared receptors. Chapter IX discussed about summary and conclusion of the thesis.

Chapter I: Introduction

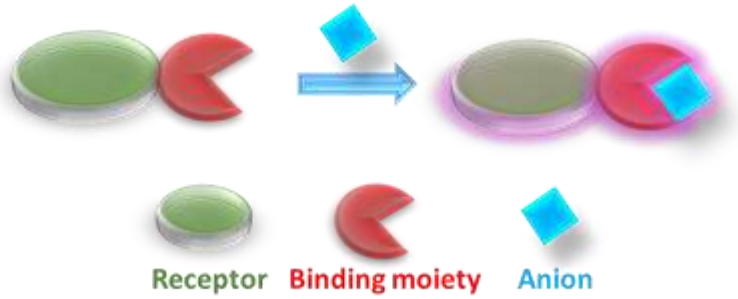
The range of supramolecular anion receptors is quite broad. Anions play a very important role in many biological and environmental processes and the necessity of anion

sensing, detection and recognition has largely grown over the years [26–29]. Hydrogen bonding is probably the most widely studied supramolecular interaction and it is crucial for the behavior of many molecules [30]. To achieve selectivity is the major issue for anion sensing studies. According to a previous report by Lakshminarayanan *et al*., when an anion interacts and is captured by a tripodal receptor, the geometrical structure of the receptor plays a crucial role in the encapsulation of the anion when the $C_2\upsilon$ symmetric receptor is tuned into a $C_3\upsilon$ receptor by an electron-withdrawing pentafluoro substitution on the phenyl rim, which increases the sensitivity and selectivity of anion sensing [31]. Theoretically, a chemo sensor's selectivity and sensitivity will increase if an electron-withdrawing moiety is substituted on the aromatic ring, according to Benjamin Hay [11].

Chapter II: Review of Literature

Chapter II discussed the literature survey about the design and development of colorimetric anion sensing is even more significant and these reports helped to develop designing the anion receptors, but a perfect sensor should fulfill the selectivity, sensitivity, colorimetric and fluorescent signal.

Chapter III: Molecular electrostatic potential (MEP) surface analysis of chemo sensors: An extra supporting hand for strength, selectivity & non-traditional interactions



Scheme 1. Design of optical anion sensor: receptor-binding unit and ICT-based optical output

Designing and preparing a synthetic receptor for a particular anion is always a challenging task for researchers since anions are having different shapes and charges. In general, an anion receptor should contain a binding unit, a signaling unit, and a proper

framework. For more than three decades, synthetic chemists used amide, amine, urea, quaternary ammonium, moieties as traditional hydrogen bonding donor units; chromophoric units were used for colorimetric response upon anion binding; chromophoric units were used for optical and spectral outputs. Even after a careful design, most of the time I failed to prepares selective and/or effective receptors for a specific anion of our interest, Scheme 1.

In this report, I used Molecular Electrostatic Potential (MEP) surface analysis software as one of the tools to visualize and support the presence of anion•••π interaction in the receptor-anion complexes. In general, the molecular electrostatic potential surface will illustrate the charge distributions of molecules three-dimensionally. These surface analyses allow us to visualize variably charged regions of a molecule. MEP surface also can interpret as a map of area of electron excess and electron deficiency.

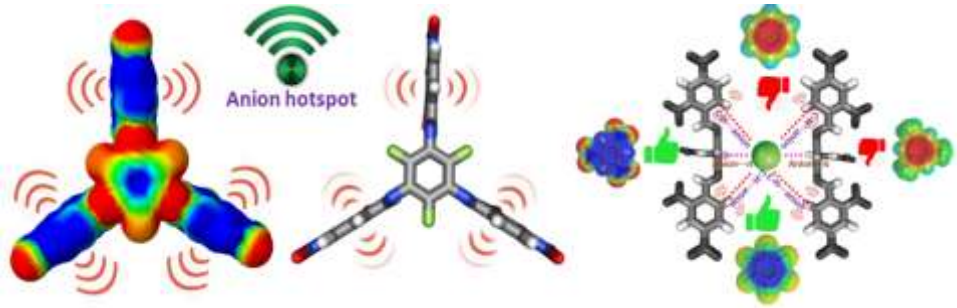


Figure 1: Molecular electrostatic surfaces (MEP) mapping of model receptor R

I have used web-based MolView application software to generate molecular electrostatic potential surface for our imine-based, electron-deficient aryl backboned tripodal model receptor R. Detailed MEP surface analysis shows the nitro substitution in the aryl moiety at 2^{nd} and 4^{th} position of each phenyl arms leave the 6^{th} C-H units more acidic which can actively participate in the anion recognition effectively through C-H•••anion interaction as shown in Figure 1. Further, the fluoro substituted electron-deficient aryl base is assisting the anion recognition process by R with its π-hole moiety through anion•••π interactions. Even though, using web-based free software MolView might give relatively less accurate results than that of high-level calculation, since it is a free, handy and easy to use, the results obtained using this software will definitely useful

in the designing the efficient synthetic receptors towards anions of interest. To the best of our knowledge this is a first report on utilization of a web-based application employed in a successful design of anion receptors through C-H••• anion and anion•••π interaction.

Chapter IV: Colorimetric and selective turn-on fluorescent sensor for cyanide via aggregation-induced enhanced emission (AIEE)

Giving the importance of design and sensing the cyanide ion, I have recently reported bipodal, tripodal-based electron-deficient selective colorimetric and turn-on fluorescent sensors for cyanide ion. From this concept, I have prepared and reported new cyanide colorimetric and turn-on fluorescent chemosensor L^1.

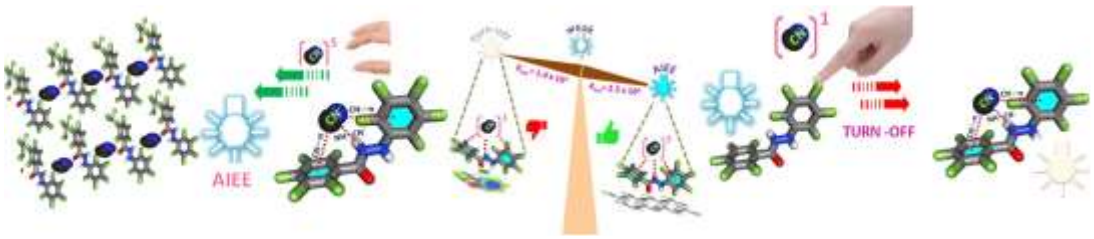


Figure 2: Graphical abstract of selective turn-on fluorescent sensor for cyanide

Naked-eye colorimetric studies show the prepared receptor is selectively sensing cyanide ions in an acetonitrile medium. The sensor L^1 shows very weak fluorescence in the acetonitrile medium. The emission intensity of L^1 gets reduced (quenching of fluorescence) upon the addition of one equivalent of cyanide. Meanwhile, the further gradual addition of more than one equivalent of cyanide onto 1:1 cyanide complex of L^1 shows remarkable fluorescence enhancement. I have tested the absorbance and emission intensity of cyanide ions in the presence of other interfering anions such as fluoride, chloride, bromide, iodide, acetate, dihydrogen phosphate, azide, bifluoride, thiocyanate, and nitrate. The experimental results show none of the anions interfered with the binding/sensing of cyanide by receptor L^1 which clearly depicts the selectivity of cyanide by L^1. The weakly emissive receptor L^1 shows drastic enhancement in fluorescence intensity upon addition of excessive cyanide ion (CN^-) which is mainly attributed due to the restriction of intramolecular rotation of 1:1 $L^1 \cdot CN^-$ complex and intermolecular aggregation of host: guest complex. This enhanced fluorescence emission is attributed due to the aggregation-induced enhanced emission (AIEE) which is depicted in Figure 2,

subsequently supported by ultraviolet-visible (UV–Vis), emission, and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopic studies. The preferential binding of cyanide by electron-deficient receptor L^1 through hydrogen bonding and anion···π interaction over benzene analog of L^1 is also analyzed with the help of molecular electrostatic potential surface analyses. To the best of our knowledge, this is the first example for selective colorimetric and turn-on cyanide sensor through AIEE mechanism. This type of fluorine-rich organic material having such an aggregation-induced enhanced emission property in response to cyanide addition will be useful to construct the new type of material for various sensory applications.

Chapter V: Electron Deficient π-Hole Assisted Hydrazone Based Probe for CN^- And F^- Recognition

Supramolecular chemistry has vast research interest along with their importance and applications. Among various directions of Supramolecular chemistry design and synthesis of receptors for anion recognition has more attention by recent researchers. Anions are playing ubiquitous roles in many living organisms and biological systems. Fluoride and cyanide is highly biologically importance and hazardous among all over anions. Anion recognition was such challenged task because of their different types of structural nature. Many reported hydrazone based receptors struggling with selectivity by non-directional hydrogen donor parts.

Receptor L^2 was designed with pi-hole assisted hydrazone to enhance the selectivity and sensitivity as I expected receptor L^2 has high sensitivity by the acidic hydrogen donor. In continues curiosity receptor L^2 was taken for anion recognition investigation by absorbance study with various anions in acetonitrile medium. To study the anion recognition capability of receptor L^2, absorption and emission properties were studied with various anions and the changes observed for (F^-, CN^-) in both absorbance and emission spectrum when no dramatic changes observed upon additions of AcO^-, Cl^-, Br^-, I^-, SCN^-, FHF^-, NO_3^- , N_3^- , $H_2PO_4^-$ ions.

Electron deficient two pentafluorophenyl moieties give directional pi-hole plane and highly acidic hydrogen available as hydrogen bond donor for anions. Structural restriction environment of pi-holes plays vital role in selectivity via anion-pi interaction.

Acidic NH proton and pi-holes capturing anion with Supramolecular interactions which was strongly associated by pi-hole assistance. Supramolecular complexes L^2+CN^-, L^2+F^- taken for stoichiometric analysis and association constant determination. Both stoichiometry and association constant of L^2+CN^- and L^2+F^- were calculated by emission studies through Stern-Volmer plot. Stern-Volmer plot drawn by F/F_0 vs Concentration of anion.

Pi-hole assistance to acidic hydrogen donor provided by pentafluorobenzene moiety which makes structural restriction to anions and it leads selectivity and electron deficient nature to receptor L^2. Anion recognition studies examined with absorption and emission spectroscopy.

Chapter VI: A Molecular Shuttlecock: Π-Hole-Induced Selective Colorimetric Tripodal Receptor for Cyanide

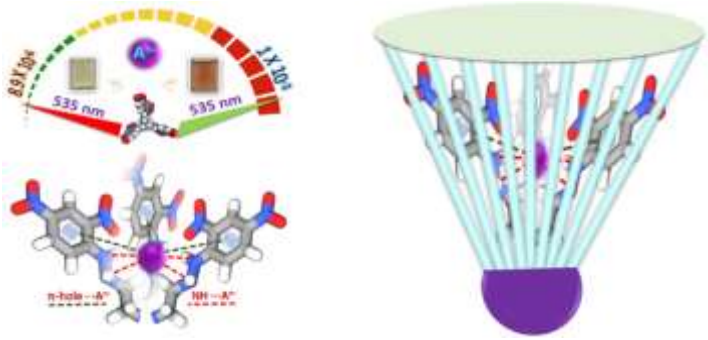


Figure 3: Graphical abstract of "Molecular Shuttlecock"

The construction of selective synthetic anion receptor is usually a challenging part in the area of anion receptor chemistry. For perfect recognition of anion by a receptor; we should have a perfect geometry of receptor. By following Ben Hay's theoretical hypothesis, in our previous reports, I have experimentally proved that the substitution of electron-withdrawing groups on aryl moieties enhanced the affection of anions by receptors. In the most of our investigations, tris (2-aminoethyl) amine [tren] and tris (3- aminopropyl) amine [tpren] have been used to construct the selective and effective receptors for various respective anions. In this report, Ihave designed, synthesized, characterized, and studied anion binding properties of novel C_{3v} symmetric tripodal receptor system L^3 for cyanide anion. Even though the receptor L^3 has tris(2-aminoethyl) amine cap in the design, I have

achieved this receptor by using tri ethanol amine as one of the precursors.

I have reported a Molecular Shuttlecock - an electron-deficient selective tripodal colorimetric receptor for cyanide anion which is depicted in Figure 3. I have achieved this selectivity with higher binding strength, by introducing electron-deficient aryl moieties in the tris(2-aminoethyl) amine-based scaffold where each arms are incorporated with –HN-NH- as hydrogen bond donor moieties. This receptor has ability to bind cyanide anion with relatively higher association constant than any other tested anions. The binding strength, limits of detection and limits of quantification towards cyanide anion is found to be 6.5 X 10^3 M, 8.7 X 10^{-8} M and 2.66 X 10^{-7} M respectively. Further, the selectivity of the receptor L^3 is supported by UV-Vis, ^{1}H-NMR, FT-IR spectroscopic and Molecular Electrostatic Potential (MEP) studies. The selectivity of receptor L^3 which caused by the dinitro substitution is further supported by studying the reference compound L^4 where all the three phenyl pendulums are backboned with electron-donating methyl groups instead of nitro group. The electron-rich (at the middle of the phenyl ring) receptor L^4 does not show any response with any tested anions including fluoride, cyanide and acetate. Inclusion of electron-withdrawing natured nitro substitution on the aromatic pendulum of the receptor L^3 creates a $\pi\cdots$holes interactions which have played a main role in framing a favorable environment for the cyanide sensing and perfect recognition in C_{3v} packet. I have also compared our receptor L^3 with other reported receptors and it is very clear that to the best of our knowledge, this is the first efficient tripodal C_{3v} symmetric receptor in terms of limits of detection reported in the literature (LoD) through UV–Vis output. The anionic complex of receptor L^3 has an open C_{3v} symmetric packet formed by three di-nitro substituted phenyl arms containing traditional –HN-NH- hydrogen bonding donor elements embedded into a tris(2-aminoethyl) amine base and the conformation is represented as “Molecular Shuttlecock”.

Chapter VII: C_{3v} symmetric tripodal molecular pocket for linear anions: Selective colorimetric detection of azide through N4-Cu-$\pi\cdots$hole interactions

Water is one of the most required substances on earth. All the plants and living natures must have water to stay alive. Apart from drinking purpose, we are consuming the water as basis for food preparation, bathing, cleaning the dresses, agriculture and cleaning

the eating utensils [32]. In the year of c. 500 CE, a well - known Tamil poet as well as a famous philosopher who known as Thiruvalluvar [33-34] was quoted in one of his 1330 couplets as,

நீர்இன்று அமையாது உலகெனின் யார்யார்க்கும்
வான்இன்று அமையாது ஒழுக்கு.

which means, “If there is no water there would be no life on earth”.

In general, it is very important to have clean water for various purposes i.e. water has to be free of germs and other contaminants [32]. Because of industrialization, the suitability of water for everyday usage is mostly poisoned with organic and inorganic species. At this juncture, it is very important to have new types of molecules or synthetic receptors which are able to identify and selectively sense those environmental polluting species.

In our early receptor designing, I have successfully used tris(2 -aminoethyl)amine and tris(3-aminoproply)amine as C_{3v} symmetric cavity-forming building blocks for making tripodal amine, amide, and urea based anion receptors. Further, I have also proved crystallographically that tris(2 - aminoethyl)amine based receptors are recognizing the anions within the tripodal cavities upon binding of anion(s). Giving the important in the need of effective and selective sensing of azide anion, I have designed and synthesized a tris(3 -aminopropyl)amine (TRPN) based C_{3v} symmetric tripodal amine receptor L^5.

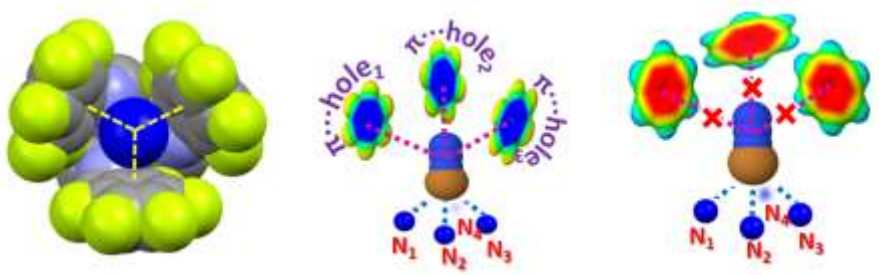


Figure 4: Graphical abstract of C_{3v} symmetric tripodal molecular pocket for linear anions

I have designed, and synthesized C_{3v} symmetry cavity making tris(3 -amino propyl)amine based receptor, L^5. It is expected that the total binding system (complex 1 + anion) should possess C_3 symmetry passing via the apical bridge head nitrogen of tris(3 -aminoproply)amine cap, central copper metals ions and azido nitrogen atoms or cyanide ion. The mono copper complex of L^5 is turned into a selective colorimetric anion receptor

for linear azide (N_3^-) anion in 7:3 acetonitrile: water solvent mixture. Systematic UV -Vis spectrometry and IR spectrometry studies reveals that, this chemo sensor is also colorimetrically recognizing the cyanide ion by its cavity via N4-Cu- π···hole interaction, these Such π···hole interaction will be possibly missing in the benzene analogue (without Penta fluoro substitution) of receptor, and hence there were no selective colorimetric responses observed upon addition of anions which is shown in Figure 4. I have visualized these models with help of molview software. Molview is a web-based application that helps scientific communities to visualize molecular structures and view their properties. To the best of our knowledge, this is the first example of a naked-eye detection of azide via cyanide displacement assay by a tripodal receptor. Presently modifying the receptor without traditional hydrogen bonding elements in order to perform our anion binding studies in 100% aqueous medium.

Chapter VIII: A Molecular Mancala: Thio-Urea based Electron-Deficient-Liquid and Solid phase colorimetric sensor for azide

Here in I have designed, prepared, characterized and studied the anion binding properties of receptor L^6. Solid state and solution state naked-eye colorimetric studies shows that the receptor is able to sense azide anion selectively in the solid as well as in the solution state. Detailed UV-Visible, ^{1}H-NMR, FT-IR, MEP surface and charge distribution calculation analyses reveal that the selectivity of this receptor towards azide is attributed due to the presence of electron withdrawing natured nitro substitutions on both the phenyl rings. The receptor L^6 binds azide anion by urea –N*H*s via hydrogen bonding interactions, non-bonding interactions such as azide···-C*H*, π-hole···anion interactions. This sensor has high affinity towards exclusively azide anion with an association constant of $9.4X10^{-3}$ M which is higher than cyanide complex which is shown in Figure 5. I have successfully tested this receptor in solid phase sensing of azide anion by mixing of both the receptor and anion in solid states. Upon solid state mixing of azide and receptor L^6, the color of the complex is instantly turned into reddish brown in color. Further spot test experiment also performed towards sensing of azide ion. To the best of our knowledge this is a first example of colorimetric sensing of azide anion both in solid and liquid state.

I just compared this preferential selectivity of receptor towards azide over other

anion with the pallankuzhi (mancala) a famous game of Tamils in Southern India. It is also known as "count-and-capture" or “sowing” game, which describes the game play. In this work, the tested anions are represented as “sow”. The cavity of Pallankuzhi represented as ligand, L^6. While adding azide/cyanide-sow into the cavity of ligand, the color of the cavity turned into reddish-brown/brown in color respectively. The cavity does not change its color upon addition of any other anion-sows.

Figure 5: Molecular Mancala (Pallankuzhi) Pictorial representation of azide selectivity by sensor L^6

Chapter IX: Summary and Conclusions

This chapter provides the summary of the results and their analysis presented in earlier chapters III to VIII.

In Chapter III, the Molecular Electrostatic Potential (MEP) surface analysis software as one of the tools to visualize and support the presence of anion•••π interaction in the receptor-anion complexes and it also can interpret as a map of the area of electron excess and electron deficiency and it also supports our spectroscopy findings.

The receptor L^1 binds CN^- stronger, on the other hand, when excess cyanide was added it increases the fluorescence intensity due to Aggregation-Induced Enhanced Emission (AIEE). Finally, selectivity between CN^- is achieved as Turn-Off and Turn-On emission outputs respectively.

The receptor L^2 was designed with two pentafluorophenyl moieties electron deficient parts which is more acidic hydrogen is present as hydrogen bond donor for anions. Structural restriction environment of pi-holes plays vital role in selectivity via

anion-pi interaction. Acidic NH proton and pi-holes capturing anion with Supramolecular interactions which was strongly associated by pi-hole assistance.

Inclusion of electron withdrawing natured nitro substitution on the aromatic pendulum of the receptor L^3 creates a π···holes interactions which have played a main role in framing a favorable environment for the cyanide sensing and perfect recognition in C_3v packet. I have prepared the reference compound L^4 where all the three phenyl pendulums are backboned with electron donating methyl groups instead of nitro group and it does not respond colorimetrically and spectrally any of other tested anions.

In chapter VII, Tris (3-amino propyl) amine, (TRPN) based C_3v symmetric tripodal molecular pocket, L^5 has been prepared and mono copper complex of L^5, having N4-Cu-π···hole as recognizing elements, becoming a potential and selective colorimetric chemo sensor for perfect linear recognition of N_3^- , generate a Cu−NNN-π···hole unit inside the tripodal pocket.

In chapter VIII, receptor L^6 binds azide anion by urea –N*H*s via hydrogen bonding interactions, non-bonding interactions such as azide···-C*H*, π-hole···anion interactions. This sensor has high affinity towards exclusively azide anion with an association constant of 9.4 X 10^{-3} M which is higher than cyanide complex. I have successfully tested this receptor in solid phase sensing of azide anion by mixing of both the receptor and anion in solid states. Upon solid state mixing of azide and receptor L^6, the color of the complex is instantly turned into reddish brown in color. Further spot test experiment also performed towards sensing of azide ion. To the best of our knowledge this is a first example of colorimetric sensing of azide anion both in solid and liquid state.

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7. LIST OF PUBLICATIONS

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